Highlights from Recent Literature

1 ANALYTICAL

1.1 Neutron Activation Analysis of Corrosion Products from Gold Coated Ear Piercing Studs

Neutron activation analysis has been applied to the determination of the elements Au, Cr, Fe, Ni and Zn released in sodium chloride solution and in a culture medium in which gold-coated studs were immersed for corrosion tests (M. Saiki, S.O. Rogero, I. Costa, O.V. Correa and O.Z. Higa, IPEN-CNEN/SP, Sao Paulo, Brazil, *Radiat. Phys. Chem.*, 1999, **55**(5-6), 753-756. The coating defects and corrosion effects on the stud surfaces were studied by SEM and energy dispersive spectroscopy analysis.

1.2 Flame Atomic Absorption Analysis of Gold Jewellery

In Spain, as in many countries, the gold content of jewellery must be hallmarked. The official methods of assay are gravimetric, cupellation (a method which is highly accurate but both time and sample consuming), potentiometric, gravimetric and volumetric. A procedure for measuring gold by flame atomic absorption in jewellery samples has been described by M.A. Llavona, M.C. Crespo, A.M. Fernandez, J.L. Ibanez, R. Zapico and B. Mishra, ed(s), Department of Materials Science, University of Oviedo, Mieres, Spain, *EPD Congr. 1999, Proc. Sess. Symp.*, 1999, 323-332. The method is based on the acid digestion of a 40 mg sample. The quantity of *aqua regia* necessary for dissolving the gold, the ideal weight of a sample in order that the error may be minimal, the effect of the acids employed, the type of material used for its storage, and the necessity of employing a buffer to avoid the ionization of the solution are described. The method proposed is simple, highly accurate and causes little damage to the jewellery.

2 CATALYSIS

2.1 Oxygen Adsorption on Well-Defined Gold Particles on TiO_2(110)

V.A. Bondzie, S.C. Parker and C.T. Campbell of the Department of Chemistry, University of Washington, Seattle, USA (*J. Vac. Sci. Technol., A*, 1999, **17**(4, Pt. 1), 1717-1720) have shown that very tiny gold particles on TiO_2 have excellent activity and selectivity in a number of oxidation reactions. The vapour deposition of gold onto a TiO_2(110) surface was studied using XPS, low energy ion scattering, LEED, and temperature programmed desorption (TPD) and it was found that gold islands can be prepared with controlled thicknesses from one to several monolayers. In order to understand at the atomic level the unusual catalytic activity in oxidation reactions of this system, oxygen adsorption on Au/TiO_2(110) was studied as a function of gold island thickness.

TPD results indicate higher desorption temperatures (645 K) for ultrathin gold particles on TiO_2(110) than for thicker particles (520-545 K). This implies that oxygen bonds much more strongly to ultrathin islands of gold, and should be able to dissociatively adsorb oxygen more readily than thick gold particles.

It was concluded that the catalytic activity in oxidation reactions demonstrated by thin (small) gold particles on titania is related to the positive influence which their stronger bonding to oxygen has on the dissociative adsorption rate of O_2.

2.2 A Kinetic and Adsorption Study of CO Oxidation over Unsupported Fine Gold Powder and over Gold Supported on Titanium Dioxide

The catalytic oxidation of CO with O_2 and adsorption of CO_2 and O_2 on gold deposited on titania (Au/TiO_2, mean diameter of gold particles 3.5 nm), TiO_2, and unsupported gold powder (mean diameter 76 nm) have been investigated by Y. Iizuka, T. Tode, T. Takao, K.Yatsu, T. Takeuchi, S. Tsubota and M. Haruta, Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Kyoto, Japan (*J. Catal.*, 1999, **187**(1), 50-58), using a closed recirculation reaction system. The oxidation reaction was found to proceed very rapidly at 253-293 K. In the same temperature range, fine gold powder was catalytically active, while TiO_2 alone was entirely inactive for the oxidation. The rate constant of CO oxidation per unit of surface area of gold was larger by two orders of magnitude for Au/TiO_2 than for gold powder. Adsorption of CO and CO_2 occurred almost instantaneously and reversibly on preoxidized Au/TiO_2, whereas a slow increase in the oxygen pressure was observed at 273 K in the absence of evacuation. A similar increase of oxygen pressure was observed from oxidized TiO_2, but gold powder did not show any increase. The increase was ascribed to the desorption of weakly adsorbed O_2 on the support surface of Au/TiO_2.

During the oxidation, dioxygen in the gas phase may be directly activated on the surface of deposited gold particles and/or on the very narrow perimeter interface between the gold and the support.

2.3 Structural Analyses and Characterization of Gold Catalysts. XAFS, Debye Functional and Mössbauer Analyses

H. Kageyama, D.A.H. Cunningham and S. Tsubota of the Osaka National Research Institute, Japan (*Osaka Kogyo Gijutsu Kenkyusho Hokoku*, 1999, **393**, 19-26, 27-35, 36-37) have reported their results on structural analysis of supported gold catalysts using XAFS, Debye functional and ^{197}Au Mössbauer spectral analysis respectively.

Au/α-Fe_2O_3, Au/$Be(OH)_2$, Au/$Mg(OH)_2$, Au/TiO_2, and Au/Al_2O_3 catalysts, at various preparation stages in course of a precipitation using $HAuCl_4$ followed by calcination and after treatment by CO and hydrogen, were subjected to Au L_3-XAFS (x-ray absorption fine structure) analyses to investigate the valence state of gold and the chemical bonding around gold atoms. For Au/α-Fe_2O_3, metallic gold is formed above 573 K, a temperature range which coincides well with the calcination temperature range for the Au-Fe coprecipitated catalyst to exhibit surprisingly high catalytic activity for CO oxidation. For Au/$Be(OH)_2$, metallic gold begins to be formed at a calcination temperature 473 K, simultaneously with development of the maximum activity for hydrogen and CO oxidations. For Au/$Mg(OH)_2$, a very stable local structure exists around the gold atoms at 473-573 K; at 523 K, the major species are gold clusters <1 nm in mean diameter and close to 13 atoms in size. For Au/TiO_2, a strong interaction occurs between the gold and the TiO_2, whereas no such interaction is present for Au/Al_2O_3. For Au/TiO_2, a significant structural change occurs at 0.1wt% with changing gold loading.

To establish whether a nanometer size gold catalyst supported on $Mg(OH)_2$ and TiO_2 undergoes a structural change to the icosahedral form to minimize its energy, a Debye function analysis (DFA) was carried out on Au/$Mg(OH)_2$ and Au/TiO_2. The main active species was gold in the icosahedral symmetry, for gold supported on $Mg(OH)_2$. The main crystal structure of gold was of fcc symmetry, in gold supported on TiO_2.

^{197}Au Mössbauer spectroscopy was used for gold supported on $Mg(OH)_2$ or TiO_2, to elucidate the origin of the catalytic activity of gold. The Au^+ species showed a good correlation with the catalytic activity in Au/$Mg(OH)_2$ catalysts, but no Au^+ species were observed for the Au/TiO_2 catalysts.

2.4 Microcalorimetry, Adsorption, and Reaction Studies of CO, O_2, and CO+O_2 over Fe_2O_3, Au/Fe_2O_3, and Polycrystalline Gold Catalysts as a Function of Reduction Treatment

N.M. Gupta and A.K. Tripathi of the Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, India (*J. Catal.*, 1999, **187**(2), 343-347) have reported their thermochemical and volumetric measurements for the adsorption and reaction of CO, O_2, and CO+O_2 on catalysts from 300 to 470 K, as a function of H_2 pretreatment. The transformation of Au/Fe_2O_3 to Au/Fe_3O_4 led to inhibited adsorption and oxidation of CO. The exposure of a reduced Au/Fe_2O_3 to CO+O_2 resulted in an O_2(ad)/CO(ad) ratio >1 as well as the reoxidation of the support and the progressive restoration of its catalytic activity. The reaction routes involved in the oxidation of CO over polycrystalline gold were different from those over the Au/Fe_2O_3 catalyst. Thus, while the simultaneous adsorption of the reactant molecules was responsible for this reaction on metallic gold, the redox mechanism involving the removal and subsequent replenishment of lattice oxygen played a role in both the Au/Fe_2O_3 and Fe_2O_3 catalysts, where the presence of gold promoted these steps.

2.5 Vapour-Phase Selective Oxidation of Aliphatic Hydrocarbons over Gold Deposited on Mesoporous Titanium Silicates in the Co-Presence of Oxygen and Hydrogen

The catalytic activity of gold deposited on Ti-MCM-41 and on TiO_2 dispersed on silica was evaluated in epoxidation of propylene and in selective oxidation of propane to acetone and of isobutane to t-butanol with H_2-O_2 mixtures under flow has been investigated by Y.A. Kalvachev, T. Hayashi, S. Tsubota and M. Haruta, Osaka National Research Institute, AIST, Ikeda, Japan (J. Catal.,1999, **186**(1), 228-233). The oxidation of propylene showed a relatively long induction period, about 1.5 h at 373 K, and becomes longer at 323 K; hydrogen consumption is about double that over Au/TiO_2/O_2. The proposed reaction mechanism involves coverage of the surface of gold particles by the hydrocarbon; at the gold surface, H_2O_2 forms from hydrogen and oxygen and migrates to free titanium sites where it is transformed to the hydroperoxo species. The hydrocarbon adsorbed on the surface of the catalyst then reacts with the hydroperoxo species to yield oxygenates.

3 CHEMISTRY

3.1 Gold(III) Reduction in Dihexyl Sulfide Extracts in the Presence of Arenes

The kinetics of reduction of gold(III) to gold(I) in organic phases after extraction from HCl-containing solutions of dihexylsulfide in heptane with admixtures of benzene, toluene, and xylene isomers at 303 K have been studied by V.V. Tatarchuk, G.A. Kostin and V.G. Torgov, Inst. Neorg. Khim., SO RAN, Novosibirsk, Russia, *Zh. Neorg. Khim.*, 1999, **44**(1), 144-147. The lowering of the reaction rate with the increase of concentration of the aromatic admixtures is explained by the specific π-interaction with the gold(III) complex. The formation constants of the adducts with the arenes were determined.

4 COATINGS, FILMS, MEMBRANES AND WIRES

4.1 Self-Assembled Monolayers of Small Aromatic Disulfide and Diselenide Molecules on Polycrystalline Gold Films

A detailed investigation of the self-assembled monolayers of diphenyl disulfide (DDS), diphenyl diselenide (DDSe), and naphthalene disulfide (NDS) on polycrystalline gold films using surface-enhanced Raman spectroscopy (SERS), XPS, and electrochemistry has been described by K. Bandyopadhyay, K. Vijayamohanan, M. Venkataramanan and T. Pradeep of the Physical / Materials Chemistry Division, National Chemical Laboratory, Pune, India (*Langmuir* 1999, **15**(16), 5314-5322). Whereas DDS dissociatively chemisorbed on gold, in both DDSe and NDS, the Se-Se and S-S bonds, respectively, are preserved upon adsorption. All of the molecules adsorb with the molecules plane perpendicular to the surface.

4.2 Self-Assembled Monolayers of CF_3-Terminated Alkanethiols on Gold

The wettability and friction of self-assembled monolayers (SAMs) of terminally fluorinated alkanethiols, $CF_3(CH_2)_nSH$ with n = 9-15, and their nonfluorinated analogues, $CH_3(CH_2)_nSH$ with n = 9-15, have been examined by M. Graupe, T. Koini, H.I. Kim, N. Garg, Y.F. Miura, M. Takenaga, S.S. Perry and T.R. Lee, Department of Chemistry, University of Houston, TX, USA, *Colloids Surf., A*, 1999, **154**(1-2), 239-244. Surprisingly, the CF_3-terminated monolayers were wetted more by water, glycerol and N,N-dimethylformamide than were the CH_3-terminated SAMs. The terminally fluorinated films, however, exhibited significantly lower surface energies. The origin of these trends is discussed. The two types of monolayers were also studied by atomic force microscopy (AFM). Compared to the CH_3-terminated SAMs, the fluorinated films revealed a three-fold increase in friction. A new model for the frictional response, which is based on the difference in size between the methyl and trifluoromethyl groups, is proposed.

5 COLLOIDS AND NANOPARTICLES

5.1 Design and Synthesis of Molecular Reactors for the Preparation of Topologically Trapped Gold Clusters

C. Roos, M. Schmidt, J. Ebenhoch, F. Baumann, B. Deubzer and J. Weis of the Institute of Physical Chemistry, Johannes Gutenberg-University, Mainz, Germany have reported {*Adv. Mater.* (Weinheim, Germany), 1999, **11**(9), 761-766} that functionalized core/shell organo-silicon micronetworks with Si-H groups bound to the core were utilized as a molecular reactor for colloid formation. The active molecular reactor is defined as a reaction vessel of nanoscopic, macromolecular dimensions providing a confined reaction volume, and actively takes part in the reaction by supplementing at least one of the reactants. A simplified scheme of the different kinetic processes (diffusion in and out, reduction, and nucleation) is given, controlling the gold colloid formation. Since reduction is strictly located in the core of microgels the formation of topologically trapped gold clusters can be observed.

5.2 Imaging and Tunneling Spectroscopy of Gold Nanocrystals and Nanocrystal Arrays

Scanning tunneling microscopy (STM) and spectroscopy (STS) have been used to determine the structural and electronic properties of thiol-passivated 29000 amu gold nanocrystals, both individually and in spontaneously formed quasi-two-dimensional arrays. These experiments were carried out by T.P. Bigioni, L.E. Harrell, W.G. Gullen, D.K. Guthrie, R.L. Whetten and P.N. First, School of Chemistry, Georgia Institute of Technology, Atlanta, GA, USA, *Eur. Phys. J. D*, 1999, **6**(3), 355-364, and performed at 300 K, 77 K, and 8 K. Even at room temperature, tunneling through these 1.7 nm nanocrystals is shown to give rise to a Coulomb blockade. At cryogenic temperatures, the spectroscopy of the nanocrystals in arrays and in isolation shows an incremental charging effect (the Coulomb staircase) and evidence is found for quantization of the electronic states.

5.3 Redox-Connected Multilayers of Discrete Gold Particles. A Novel Electroactive Nanomaterial

D.I. Gittins, D. Bethell, R.J. Nichols and D.J. Schiffrin of the Department of Chemistry, University of Liverpool, UK (*Adv. Mater.* (Weinheim, Germany), 1999, **11**(9), 737-740) report a new dithiol-functionalized viologen, N,N-di (10-mercapto-decyl)-4,4'-bipyridinium dibromide, synthesized from potassium thioacetate and 1,10-dibromodecane in refluxing THF followed by reaction with 4,4'-bipyridyl. It has been used to prepare films of chemically linked gold nanoparticles using the viologen as a redox-active linker in 3D structures. The layers were assembled by alternate dipping of a spheroidal gold electrode in methanol solutions of the viologen and gold nanoparticle sols in toluene. The cyclovoltammetric characteristics of the layers and multilayers were investigated and further characterized by UV spectroscopy. The films were air-stable and showed no degradation, even after thousands of electrochemical cycles and several months of storage. Thus, the viologen dithiol can be used to prepare a new type of stable electroactive material containing discrete gold nanoparticles. The redox linker group could be reversibly electrochemically addressed and its presence did not hinder the electron transfer through the nanostructured material.

5.4 Control Over Size and Density of Sub-5 nm Gold Dots by Retarding-Field Single Ion Deposition (RSID)

Gold dots of 2.5 nm mean diameter and 0.8 nm standard deviation have been fabricated successfully on chromium oxide thin films using a retarding-field single ion deposition (RSID) technique (M. Hori, T. Goto, R.G. Woodham and H. Ahmed of the Department of Quantum Engineering, Nagoya University, Nagoya, Japan, *Microelectron. Eng.*, 1999, **47**(1-4), 401 - 403). The sub-5 nm gold dots have also been also formed on PMMA and diamond-like carbon (DLC) films by controlling the landing energy and dose of gold ions. The formation of single electron devices, quantum dots, nanopillars and other nano-scale device structures is proposed using the RSID technique.

6 ELECTROCHEMISTRY

6.1 Enantioselective Oxidation of Amines on a Gold Electrode Modified by a Self-Assembled Monolayer of a Chiral Nitroxyl Radical Compound

The enantioselective voltammetric behaviour of chiral amines at gold electrodes modified with a mixed monolayer of chiral nitrosyl radical compound and hexadecanethiol has been described by Y. Kashiwagi, K. Uchiyama, F. Kurashima, J.I. Anzai and T. Osa, Graduate School of Pharmaceutical Sciences, Tohoku University, Sendai, Japan, *Anal. Sci.*, 1999, **15**(9), 907-909.

6.2 Cyclic Voltammetric Studies on the Reduction of a Gold Oxide Surface Layer

The cathodic reduction of a stationary surface layer of gold compounds formed anodically on a gold electrode in 0.5 M sulfuric acid solution at E = 1.7 V, *ie* prior to O_2 evolution, was investigated by K. Juodkazis, J. Juodkazyte, B. Sebeka and A. Lukinskas, Laboratory of Precious Metals Electrochemistry, Institute of Chemistry, Vilnius, Lithuania, *Electrochem. Commun.*, 1999, **1**(8), 315-318. With the initial amount of gold oxide on the electrode surface being constant, Tafel behaviour was observed for the cathodic process of the reversible metal / metal oxide electrode. The reversibility of the cathodic process may be determined by the equilibrium of the following surface reaction: $Au.H_2O + 2\ H_2O \rightarrow (Au(OH)_3)_s + 3\ H^+ + 3\ e^-$ where $Au.H_2O$ represents the gold surface atoms with electrostatically adsorbed H_2O, and $(Au(OH)_3)_s$ is $Au(OH)_3$ in the form of the surface layer. This equilibrium may exist at the interface only when the $Au(OH)_3$ layer is present on the electrode surface. The equilibrium potential of this reaction was evaluated as 1.28 ± 0.01 V.

6.3 Localized Investigation of Coarse Grain Gold with the Scanning Droplet Cell and by the Laue Method

A coarse grain gold specimen was studied by A.W. Hassel and M. Seo of the Laboratory of Interfacial Electrochemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Japan (*Electrochim. Acta*, 1999, **44**(21-22), 3769-3777) using the scanning droplet cell (SDC). Voltammograms on single grains were obtained and show the shape which is characteristic for a (111) single crystal plane.

In addition, the potential dependence of the capacity was recorded. The crystallographic orientation of each grain was determined by Laue x-ray back scattering. All grains have a (111) orientation but different azimuth angles. This angle was determined quantitatively for different grains.

6.4 Electroless Gold Plating of 316 L Stainless Steel Beads

P. Lam, K. Kumar, G.E. Wnek and T.M. Przybycien of the Howard P. Isermann Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY, USA (*J. Electrochem. Soc.*, 1999, **146**(7), 2517-2521) have described an electroless gold plating process for particulate 316L stainless steel. The process is based on a mildly acidic Au-Na thiosulfate/ascorbic acid plating solution and is performed under an inert environment at room temperature. The process affords a gold deposition efficiency of *ca* 50% as inferred from a modified $SnCl_2$-based spectrophotometric assay for gold ion concentration.

Successful deposition of gold depended on the removal of the thin, passivating surface oxide layer on the stainless steel; this was accomplished by an initial cleaning step with 2 M HCl. *In situ* cyclic voltammetry experiments on a stainless steel electrode and atomic force microscopy scans on small coupons were used to further characterize the oxide removal and gold deposition reactions.

7 ELECTRONICS

7.1 Bonding of Gold Wire to Printed Circuit Boards with Electrolessly Deposited Nickel/Immersion Gold Metallizations

Printed circuit boards metallized with electroless nickel and immersion gold were selected from current production output of several manufacturers, and their bondability with gold wires tested (H. Osterwinter, J. Fessmann, V. Von Arnim, U. Voller, J. Eisenlohr and M. Bohm, Goppingen, Germany, *Prod. Leiterplatten Syst.*, 1999, **1**(6), 837-843). In the as-delivered condition, gold wire-bonding was either not possible or unsatisfactory. After using a prescribed combination of aqueous and plasma cleaning cycles, the surfaces were readily gold wire-bondable in a manner suited to production.

7.2 Study on the Charge Transfer Mechanism at Static State in Gold-Doped n-Type Silicon using Statistical Method

Y. Yan of the Department of Physics, Xiamen University, P.R. China (*Guti Dianzixue Yanjiu Yu Jinzhan*, 1999, **19**(2), 226-230, has demonstrated that the concentration of carrier and the charge density on energy levels of impurities in the n-type silicon doped gold vary with temperature, using statistical methods. The charge transfer mechanism at static state is approached. The results support the view that the gold acceptor level and the gold donor level in silicon can essentially originate from the same gold impurity.

8 MATERIALS SCIENCE

8.1 Method for Preparing Gold-Containing Pigments for Glazes

This new method, patented by D. Vollath, S. Heidenreich and F. Wacker, Forschungszentrum Karlsruhe GmbH, German Patent DE 19824440 C1 990902, involves the preparation of a vaporizable gold compound, a vaporizable compound of another metal capable of forming an oxide or nitride melting at a temperature higher than the melting point of gold, and an O- and/or N-containing reaction gas, introducing the compounds and gas into a first microwave plasma whereby gold cluster-coated nuclei are formed from the nitrides and/or oxides, and subjecting the nuclei to a heat treatment at 150-300°C to obtain the desired colour. The pigments are suitable for manufacturing red glass, *eg*, ruby glass.

$AlCl_3$-containing 10mol% $AuCl_3$ was mixed with argon containing 10vol% oxygen and exposed to microwaves of 915 MHz at 2 kW and 450°C and 20 mbar. Heat treatment at 160°C gave the desired red colour.

9 METALLURGY

9.1 Low-Temperature Diffusion of Gold in Germanium under the Influence of Atomic Hydrogen

V.M. Matyushin of the Zaporozhe State Technical University, Zaporozhe, Ukraine (*Tech. Phys.*, 1999, **44**(7), 804-806) has investigated the diffusion of gold in germanium under the influence of the energy released by the recombination of hydrogen atoms to form molecules. Crystals of n-type germanium with gold films ($d = 1 \times 10^{-7}$ m) are exposed to atomic hydrogen for various times (up to 104 s) at temperatures close to room temperature. The diffusion of gold in the germanium is analysed by laser mass spectrometry, and also by measuring the surface resistance, the minority carrier lifetime, and the IR transmission spectra. Mechanisms are proposed for the stimulation of heterodiffusion and accompanying processes.

9.2 Method for Processing Experimental Data on Concentration- and Temperature-Dependence of Thermodynamic Activity of Gold-Silver Solid Solutions

This method proposed by E.A. Soldatov, Mosk. Gos. Univ., Moscow, *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1999, **40**(4), 275-276, allows the determination of thermodynamic activity as a function of concentration and temperature for arbitrary binary solutions. The three stages of the determination are: (i) elimination of trivial dependencies using mutual energy exchange; (ii) elimination of experimental points outside the Gaussian distribution of deviations of the transformed dependence; (iii) determination of the important energy exchange parameters. The mutual exchange energy for the system Au-Ag depends on the molar concentration and temperature.

10 REFINING

10.1 Pressure Hydrometallurgy Need No Longer be Regarded with Trepidation for the Treatment of Gold and Base Metal Ores and Concentrates

P.G. Mason, J.W. Gulyas, and B. Mishra (eds), Highlands Pacific Limited, Brisbane, Australia (*Congr. 1999, Proc. Sess. Symp.*, 1999, 585-616) have reviewed the operation of the numerous pressure oxidation and pressure leach plants installed throughout the world over the last 15 years. The technology is no longer regarded with awe and trepidation as plants designed to treat a wide range of feedstocks continue to be successfully brought on line. Important aspects of the design of such plants include feed preparation, slurry pumping, heating and heat recovery, pressure control and let-down, vessel design, safety and provision of associated services.

10.2 Environmental Chemical Aspects of Gold Recovery Processes

F. Korte, Technische Universität Munchen Institut für Chemie Lehrstuhl für Okologische Chemie, Freising-Attaching, Germany, *GIT Labor-Fachz*, 1999, **43**(10), 1082-1083 discusses environmental pollution by gold mining and recovery operations. Topics include: ecological chemistry, current consideration of ecosystems, global environmental problems, and gold recovery processes, *eg* amalgam processes, gold cyanide leaching, flotation, and gravity separation.